3. CHEMICAL AND PHYSICAL INFORMATION

3.1 CHEMICAL IDENTITY

Information regarding the chemical identity of white phosphorus is located in Table 3-l.

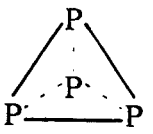
3.2 PHYSICAL AND CHEMICAL PROPERTIES

Information regarding the physical and chemical properties of white phosphorus and white phosphorus smoke is located in Table 3-2.

Elemental phosphorus exists in several allotropic forms (Van Wazer 1982). The best known and most important commercially is the a-white phosphorus whose properties are given in Table 3-2. Commercial white phosphorus is 99.9% pure, with a slight yellow color caused by traces of red phosphorus impurities. Hence, white phosphorus also is known as yellow phosphorus. When a-white phosphorus is cooled below -79.6°C, P-white phosphorus forms. Other important solid allotropes of phosphorus are red and black phosphorus (Van Wazer 1982).

The U.S. Army uses at least two phosphorus-based smoke/obscurants for training and testing activities (Shinn et al. 1985). One such agent is white phosphorus/felt (WP/F), and the other is red phosphorus/butyl rubber (Spanggord et al. 1985). WP/F consists of 75-80% white phosphorus solidified into a cellulose (felt) matrix (20-25%). When WP/F is burnt, besides unburnt white phosphorus, the smoke consists primarily of oxidation and hydrolysis products of phosphorus. For example, when white phosphorus burns in air it produces oxides of phosphorus including phosphorus pentoxide (P_4O_{10}, and phosphorus trioxide (P_40_6). These oxides react with moisture present in air to form a number of phosphorus-containing acids, such as orthophosphoric acid (H_3PO_4), pyrophosphoric acid ($H_4P_2O_7$), orthophosphorus acid (H_3PO_3), hypophosphorus acid (H_3PO_2), polyphosphoric acid of the general formula $H_{n+2}P_nO_{3n+1}$, where n=2-8, and a homologous series of linear and cyclic P_6-P_{16} polyphosphates (Spanggord et al. 1983; Tolle et al. 1988). The composition of white phosphorus smoke will change with time (Spanggord et al. 1988). In the absence of stoichiometric quantities of oxygen, phosphine (PH_3) may form in WP/F smoke from the reaction of unreacted phosphorus with moisture in air (Spanggord et al. 1983).

TABLE 3-1. Chemical Identity of White Phosphorus

Characteristic	Information	Reference
Chemical name	White phosphorus	CAS 1995
Synonym(s)	Yellow phosphorus, phosphorus tetramer	CAS 1995
Registered trade name(s)	No data	
Chemical formula	P_4	CAS 1995
Chemical structure		Spanggord et al. 1985
Identification numbers:		
CAS registry	7723-14-0	CAS 1995
NIOSH RTECS	TH3500000	RTECS 1995
EPA hazardous waste	D003	HSDB 1995
OHM/TADS	7216855	RTECS 1995
DOT/UN/NA/IMCO shipping	UN1381	RTECS 1995
HSDB	1169	HSDB 1995
NCI	No data	

CAS = Chemical Abstracts Services; DOT/UN/NA/IMCO = Department of Transportation/United Nations/North America/International Maritime Dangerous Goods Code; EPA = Environmental Protection Agency; HSDB = Hazardous Substances Data Bank; NCI = National Cancer Institute; NIOSH = National Institute for Occupational Safety and Health; OHM/TADS = Oil and Hazardous Materials/ Technical Assistance Data System; RTECS = Registry of Toxic Effects of Chemicals Substances

TABLE 3-2. Physical and Chemical Properties of White Phosphorus

Property	Information	Reference
Molecular weight	123.895	Budavari et al. 1989
Color		
Pure form	Colorless to white	Budavari et al. 1989
Technical form	Yellow	Van Wazer 1982
Physical state	Waxy solid	Budavari et al. 1989
Melting point	44.1°C	Budavari et al. 1989
Boiling point	280°C	Budavari et al. 1989
Density:		
at 20°C	1.82 g/cm^3	Weast 1985
Odor	Garlic-like	HSDB 1993
Odor threshold:		
Water	No data	
Air	No data	
Solubility:		
Water at 15°C	3 mg/L	Weast 1985
Organic solvent(s)	Soluble in alkali, ether, chloroform, benzene, toluene	Weast 1985
Partition coefficients:		
Log K_{ow}	3.08	Spanggord et al. 1985
Log K_{oc}	3.05 (estimated)[a]	
Vapor pressure:		
at 20°C	0.025 mmHg; 0.026 mmHg	Farr 1950; HSDB 1993
Henry's law constant:		
at 20°C	2.11×10^{-3} atm·m^3/mol; 1.36×10^{-3} atm·m^3/mol[b]	Spanggord et al. 1985
Autoignition temperature	30°C (moist air); 35–46°C (dry air)	NSC 1990
Flashpoint	Spontaneous in air	Sax 1984
Flammability limits	No data	
Conversion factors	1 ppm = 5.150 mg/m^3 at 20°C	
Explosive limits	No data	

[a]Estimated from the regression equation given by Lyman (1982). The experimental values (range 2.56–2.77) of Spanggord et al. (1985) are unreliable due to the reactivity of white phosphorus.

[b]Estimated from the ratio of vapor pressure at 20°C and the water solubility at 15°C.

Reactions of white phosphorus that lead to the formation of some typical products are listed below (Cotton and Wilkinson 1980; Spanggord et al. 1985).

$P_4 + 3O_2 \rightarrow P^{+3}_4 O_6$	(phosphorus trioxide)
$P_4 + 5O_2 \rightarrow P^{+5}_4 O_{10}$	(phosphorus pentoxide)
$P_4O_{10} + 6H_2O \rightarrow 4H_3P^{+5}O_4$	(orthophosphoric acid)
$P_4O_{10} + 2H_2O \rightarrow 4HP^{+5}O_3$	(metaphosphoric acid)
$P_4O_{10} + 4H_2O \rightarrow 2H_4P^{+5}_2 O_7$	(pyrophosphoric acid)
$P_4O_6 + 2H_2O \rightarrow 4HP^{+3}O_2$	(metaphosphorus acid)
$P_4O_6 + 6H_2O \rightarrow 4H_3P^{+3}O_3$	(orthophosphorus acid)
$P_4 + 8H_2O \rightarrow 4H_3P^{+3}O_2 + 2H_2$	(hypophosphorus acid)
$4H_3PO_3 \rightarrow H_3P^{+5}O_4 + P^{-3}H_3$	(phosphine by disproportionation)
$3H_3PO_4 \rightarrow H_5P^{+5}_3 O_{10} + 2H_2O$	(triphosphoric acid)

Organic constituents that may be found in ppb levels in WP/F smoke include methane, ethylene, carbonyl sulfide, acetylene, 1,4-dicyanobenzene, 1,3-dicyanobenzene, 1,2-dicyanobenzene, acetonitrile, and acrylonitrile (Tolle et al. 1988). Since white phosphorus contains boron, silicon, calcium, aluminum, iron, and arsenic in excess of 10 ppm as impurities (Berkowitz et al. 1981), WP/F smoke also contains these elements and possibly their oxidation products. The physical properties of a few major compounds that may be important for determining the fate of WP/F smoke in the environment are given in Table 3-3.

Table 3-3. Physical Properties of Major Compounds in White Phosphorus Smoke[a]

Property	Phosphorus trioxide	Phosphorus pentoxide	Ortho-phosphorus acid	Ortho-phosphoric acid	Phosphine
Molecular formula	P_4O_6	P_4O_{10}	H_3PO_3	H_3PO_4	PH_3
Molecular weight	219.89	283.89	82.00	98.00	34.00
Color	White	White	Yellow	Colorless	Colorless
Physical state	Solid	Solid	Solid	Liquid or solid	Gas
Melting point	23.8°C	340°C[b]	73.6°C	42.35°C	-133.5°C
Boiling point	173.8°C (in N_2)	Sublimes at 360°C[b]	Decomposes at 200°C	Decomposes at 213°C	-87.4°C (auto-ignites 37.7°C[b])
Density, g/cm^3	2.135 at 21°C	2.39	1.651 at 21.2°C	1.834 at 15°C	1.529 g/L
Odor	No data	No data	No data	No data	Garlic-like[b]
Solubility:					
Water	Decomposes to H_3PO_3 at 20°C	Decomposes to H_3PO_4 at 20°C	694 g/100 mL at 40°C	548 g/100 in cold water	0.398 g/L at 17°C; 0.381 g/L at 25°C
Organic solvent(s)	Soluble in carbon dioxide, chloro-form ether	Insoluble in acetone	Soluble in ethanol	Soluble in ethanol[b]	Soluble in ethanol, ether
Partition coefficients:					
Log K_{ow}	Not relevant	Not relevant	Not relevant	Not relevant	No data
Log K_{oc}	Not relevant	Not relevant	Not relevant	Not relevant	No data
Vapor pressure	No data	No data	No data	No data	760 mm at -87.4°C
Henry's law constant at 20°C	No data	No data	No data	No data	0.09 atm·m^3/mol[c]

[a]All information obtained from Weast 1985 except where noted
[b]Hawley 1981
[c]Spanggord et al. 1985